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Studies of Interfacial Chemistry between Metals and Their Effect on Electronic Systems

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Introduction

This report summarizes research performed at Stanford from October 1, 1985 to September 31, 1988 under DARPA/ONR contract No. N00014-83-K0073 entitled "Study of Interfacial Chemistry between metals and III-V semiconductors and Their Effect on Electronic Systems". The very large scope of research done under this contract resulted in 83 publications in the major scientific literature. The list of publications is enclosed with this report. On the basis of data obtained in this program six students at Stanford University received their PhD degrees under directions of Profs. W. E. Spicer and I. Lindau. Two others completed the experimental part of their dissertations.

The technical problem was to study the interfacial chemistry on the metal/III-V semiconductor systems and their influence on electronic properties of interfaces. The study was concentrated on GaAs and to a lesser extent InP - two representative III-V semiconductors of foremost technological interest. The studies also included oxidation partly because of the presence of oxides at interfaces of practical devices, and studies of III-V semiconductor heterojunctions which are very closely related to the problems investigated in this proposal. Also, some amendments of the program were implemented to touch on current developments in the field of III-V semiconductor interfaces. A broad range of laboratory techniques has been used with particular emphasis on photoemission spectroscopy for thin overlayers and I-V and C-V electrical measurements for thick metallic overlayers. The work in thick junctions largely benefited from cooperations with other groups. In particular, cooperation with the Berkeley group of Prof. E. Weber and Dr. Z. Liliental-Weber which performed microanalytical studies (TEM, EDX etc.) on devices prepared and characterized by our group has to be acknowledged. Our investigation of chemical reactions spanned a broad range of temperatures from liquid nitrogen to high temperature anneals. More precisely, temperatures at which the interfaces were produced or annealed often served as way of reaction control (through control of reaction kinetics).

In this way we were able to study the influence of chemical reactions on the electronic properties of the devices. Our finding can be summarized as follows:

1. At low temperatures, where reactions are limited and at higher temperatures for nonreactive interfaces, the Schottky barrier at the metal semiconductor interfaces is mainly determined by metal induced gap states (MIGS).

2. For mildly reactive interfaces the interplay between MIGS and metallization induced defects determines electrical properties of the junction, with the defect states becoming dominant for strongly reactive systems.

3. The key defect for reactive GaAs interfaces has been identified as As_{Ga} antisite (double donor) with states at 0.75 eV and 0.5 eV above the valence band maximum (VBM) compensated by an acceptor (most likely Ga_{As}) at lower energy. The energies of the interfacial defects are found to be consistent with the energies of bulk EL2 traps in GaAs.

4. The interfacial reaction affects the Schottky barrier height by changing the As/Ga ratio on the semiconductor side of the interface. For example, reactions which consume As, decreases As_{Ga}/Ga_{As} ratio and increases (decreases) barrier height on n-type (p-type) GaAs by moving Fermi level at the interface toward low energy compensating acceptors.

Findings 4 and 5 constitute the thrust of the Advanced Unified Defect Model (AUDM) proposed by us as a result of the studies done under this proposal. As described before in the quarterly reports this model explains a broad range of data for clean GaAs surfaces and GaAs interfaces. The key factor defining Schottky barrier height is chemistry controlled stoichiometry at the interface (As/Ga ratio). During the process of those studies a broad range of GaAs and InP interfaces have been characterized in terms of chemical reaction and growth morphology in correlation with band bending. These results have been reported in a number of publications (see publication list). Only some of the findings will be summarized below in this report.

Summary of results.

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I. Chemical reactions on III-V semiconductor surfaces (thin overlayers)

The characterization of chemical reactions of III-V semiconductor interfaces was the key problem addressed by this program. In order to get a good understanding of chemical trends, a broad range of overlayers deposited in a controlled fashion on GaAs and InP surfaces has been investigated by PES. The systems studied included overlayers of:

1. Transition (refractory) metals (Cr, Mn, Ti, Co); see Ref. 7, 16, 32, 55, 67 (in the enclosed list of publications)
2. Near noble transition metals (Ni, Pd, Pt); Ref. 8, 15, 38, 53.
3. Noble metals (Cu, Ag, Au); Ref. 1, 18, 43, 44, 75, 80
4. Column III metals (Al, Ga, In, Tl); Ref. 3, 4, 19, 23, 27, 39, 41, 42, 48, 59,
5. Rare earth metals (Yb); Ref 25 and 28
6. Homopolar semiconductors (Si, Ge); Ref 29, 45, 52, 56, 68, 70, 77
7. Nonmetallic overlayers of column V elements (As, Sn, Sb); 55, 72, 73

Because the interfacial reactions are in general very complex and a full account of the results cannot be attempted in this report due to space limitations, we will only very briefly summarize the main results. More information is provided in the literature and in particular in Ref. 12, 20, 21, 24, 37, 60, 61, 62, 63, and 74 which are more general in nature. Many of the systems studied have to be considered on a case by case basis. However, the unprecedented scope of the interfacial chemistry studies performed by our group and other workers (in particular J. Weaver's group) resulted in some general conclusions. We draw strongly on these experiments in the Advanced Unified Defect Model of Schottky barrier formation recently developed by our group and described below. This model considers the relative movement of As in the process of metallization as the most important factor controlling the height of the rectifying barrier.

Summary of PES studies in chemistry.

1. Transition and near noble metals with partially filled d shells are the most reactive overlayers. In general, overlayers of these metals grow in a reacted laminar fashion and reactions involve both anions and cations of the substrate. Reactions to the first approximation are adequately described by bulk thermodynamical properties. These interfaces are often abrupt.

2. From the noble metals Ag is found to be the least reactive. For Cu and Au, reactions are observed at RT and involve mostly the anion or cations of the substrate for Cu and Au respectively. Noble metals, as well as column III metals, have a tendency to form clusters on III-V semiconductor surfaces.

3. Column III metals and homopolar semiconductor (Ge, Si) overlayers covalently bonded to the III-V semiconductor surfaces are only moderately reactive, while nonmetallic column V elements are nonreactive, grow in laminar fashion, and often form abrupt epitaxial overlayers (Sb). For these elements, (as well as for noble metals) reactions are strongly temperature dependent. Interfacial exchange reaction or interdiffusion for these species may lead to ohmic behavior through the formation of graded heterojunctions (In) or subsurface doping (Si, Ge).

4. Interfacial reactions prevent a free movement of As or P through the metal overlayer. For InP phosphorous is trapped at the boundary. For GaAs some As diffuses to the outer surface but large amounts of As also make the boundary As rich.

5. Cations of GaAs or InP show a gradient of outdiffusion to the outer surface. A model calculation using the Born-Haber cycle shows that upper parts of the metallization contain diluted amounts of Ga or In.

5. For both GaAs and InP there appears a correlation between reactions and band bending. However, we find that the relative amount of As or P rather than strength of the interfacial bond (as suggested by some workers) is responsible for this. In particular, for InP, band

bending has been shown to depend on the symmetry of outdiffusion, and, for GaAs, the movement of As has been shown to be a key observation leading to AUDM.

II. Electrical and microanalytical characterization of GaAs interfaces

In order to test the currently popular models of Schottky barrier formation, we have performed an extensive study of thick metal film (~1000Å) diodes. Submonolayer coverages of impurities are capable of establishing a barrier, altering the chemistry at the interface and significantly affecting the current transport mechanism in electrical device measurements. Therefore, in this study diodes were produced on clean-cleaved GaAs (110) and InP(110) interfaces under UHV conditions with *in-situ* metal deposition.

Near ideal electrical characteristics of metal/n-GaAs Schottky barriers are consistently found. Using thermionic emission theory, the barrier heights were found to fall in a relatively narrow range between 0.67 eV for Cr to 0.92 eV for Au. The same pinning energies were found for p-GaAs devices. The measured barrier heights for these thick film (~1000Å) diodes fall within experimental error of the values obtained at submonolayer coverages from the PES studies.

The structure of such well-defined Ag, Al, Au, Cr and Ti contacts on GaAs has been investigated by high resolution and analytical transmission electron microscopy. In all cases the metal/semiconductor interface was atomically abrupt. In the representative case of the Au/GaAs interface the last 3 to 5 atomic layers near the interface are highly reconstructed indicating a highly strained and defected region at the metal/semiconductor interface.

Analytical TEM EDX results of all of the systems studied showed that the region within ~ 100Å of the interface is slightly As rich when compared to the bulk. This As-rich condition near the interface is also found to diminish with time under the illumination of the electron beam, while no change in the temporal dependence of the As-concentration in the

bulk is found. This suggests that a less tightly bound form of As in significant concentrations occurs at or near the interface.

In order to study the effects chemical reactions between the metal and the GaAs can have on the Schottky barrier height, we have carried out an annealing study of several of the systems. In an open system, Au reacts exclusively with Ga, forming an alloy of Au and Ga. For the case of the UHV-cleaved surfaces, TEM micrographs and surface analysis by laser ionization have shown that the concentration of Ga in the Au is sufficiently small that no new crystallographic phases are formed. After annealing, the presence of a higher concentration of Ga in the crystalline Au phase and a significantly larger quantity of As released by the reaction and trapped near the interface has been detected. A significant decrease in the barrier height of the Au/n-GaAs diode is found upon annealing.

In contrast, Al reacts almost exclusively with As to form the exchange reaction $xAl+GaAs \rightarrow Al_xGa_{1-x}As + xGa$. Analytical TEM EDX results indicate that the amount of excess As near the interface is decreased upon annealing. A significant increase in the barrier height of the Al/GaAs diodes is also found. It is important to note that the increase in barrier height for diodes formed on n-type material for both the Al/GaAs and Al/InP system was found to be within experimental error of the decrease in the barrier height of diodes formed on p-type material. This indicates that the changes in barrier height can be attributed to a change in Fermi-level pinning position at the interface, rather than to the increased bandgap of the alloy formed at the interface. Ti is expected as well to react primarily with the As, and as in the case of Al it is indeed found to increase its barrier height upon annealing.

We also performed a systematic study of the annealing-induced changes in the barrier height of Schottky barrier diodes fabricated on atomically clean and contaminated surfaces. Al, Ag, Au, and Cr/GaAs(11) diodes were fabricated by *in situ* deposition on clean n-type GaAs(110) surfaces prepared by cleavage in ultrahigh vacuum and on contaminated surfaces prepared by cleavage and exposure to the atmosphere for ~ 1-2 h.

This study demonstrates that the as-deposited barrier height and the annealing-induced changes in the barrier height of diodes formed with an interfacial layer of contamination are distinctly different from the characteristics of diodes formed on clean semiconductor surfaces. The presence of an interfacial layer of contamination is found to significantly degrade the stability of the diode's barrier height due to annealing.

In summary of this section, our electrical study of metal/n-GaAs diodes found strong correlations between the expected and the observed stoichiometry and changes in barrier height upon annealing. In all cases, an increase in the excess-As near the interface is found to correlate with a decrease in the barrier height, whereas a decrease in the excess-As near the interface correlates with an increase in the barrier height.

III. The Advanced Unified Defect Model for GaAs surfaces

The observed defects at the metal/semiconductor interface, their correlation with the Schottky barrier height and the stoichiometry-related changes of barrier height upon annealing make it very difficult to explain the Fermi level pinning mechanism exclusively in terms of the electronic structure of a "perfect" metal/semiconductor interface. Although metals in intimate contact with a semiconductor may result in new, metal-induced electronic states in the bandgap, the experimentally observed pinning positions often appear to be dominated by crystal defects present in the semiconductor near the interface.

As pointed out in the previous section, for a wide variety of metal contacts deposited under ultrahigh vacuum conditions on GaAs, only a very narrow range of pinning positions is observed. This indicates, that the defects involved in Fermi level pinning are indeed well-defined intrinsic deep level point defects rather than unspecific metal-related defects. The possible candidates for such defects have to be thermally stable, intrinsic lattice defects.

The surprising coincidence of the experimentally determined energy levels of the As_{Ga} antisite defect at $E_v + 0.52$ eV and E_c-0.75 eV with the Fermi level pinning positions

lead very early to the suggestion that the defects dominating the Fermi level pinning mechanism might indeed be anion antisite defects. Such double donor defects can easily pin the Fermi level of p-type compound semiconductors, but for pinning of n-GaAs they require the additional presence of compensating acceptors. These are identified as Ga_{As} antisite defects.

Spectroscopic and microanalytical data show that the process of metal deposition by evaporation or sputtering is likely to heavily distort the first few monolayers of a semiconductor, mainly due to the latent heat released upon condensation of the metal particles. This near-surface disturbance will result in the presence of a large concentration of vacancies and interstitials of both types of atoms in a compound crystal. However, these simple point defects are not stable at or slightly above room temperature and therefore can not play an important role in the stabilization of the interfacial Fermi level. Nevertheless, whenever an interstitial host atom recombines with a vacancy of the other type, a thermally stable antisite defect is formed. The stability of antisite defects at temperatures up to about 950°C correlates indeed very well with the highest temperature at which the best, refractory metal-related Schottky contacts on GaAs maintain their rectifying behavior.

To a first approximation, an equal number of antisite defects on both sublattices can be expected to be formed. However, two mechanisms will in most cases result in the preference of anion-rich antisite defects. First, bulk crystal growth is commonly performed under As-rich growth conditions in order to balance the As-loss during crystal growth. Secondly, As is the volatile component, so that the strain field associated with a surface or interface can further promote the accumulation of As near such a distortion. Scanning Auger microscopy detected directly the formation of As-clusters on a freshly cleaved surface. This situation is similar to the strain field surrounding a dislocation, and indeed various TEM studies have directly confirmed the presence of As-precipitates at dislocations and As-rich crystal stoichiometry surrounding a dislocation.

The advanced unified defect model (AUDM) assumes, that the presence of a higher concentration of mobile As, as compared to mobile Ga, is the reason for the dominance of As antisite defects over Ga antisite defects, but the presence of both defects seems to be evident from the observed Fermi level pinning processes. If annealing results in further As accumulation in the semiconductor near the interface, the increased dominance of the As_{Ga} results in an increase of the number of donors and pinning closer to midgap. If the annealing reaction reduces the amount of excess As near the interface, the opposite occurs and pinning is closer to the valence band.

The role of surface stoichiometry and interfacial lattice disorder for the Fermi level pinning process is as well evident from the results of two most recent experiments. According to the AUDM, an increase in As relative to Ga would produce Fermi level motion toward the CBM, i.e. reduced Schottky barrier height on n-GaAs; whereas, the converse would be true for a reduction in the As/Ga ratio. For most of the cases uncovered, this is found to be the case. Examples follow.

MBE growth is usually done under As-rich conditions. For the pure but As-rich GaAs surfaces, (e.g. no-metal or oxygen on the surface), the Fermi level pinning position corresponds very well to the energy levels of the AUDM. Furthermore, the E_f levels move as predicted if the As excess is increased or decreased. In the unusual cases where Ga-rich MBE surfaces have been prepared, the surface Fermi level appears to be unusually close to the VBM as would be expected from the AUDM if the ratio of Ga_{As}/As_{Ga} antisite becomes greater than unity.

Another possible way of increasing the Ga_{As} ratio would be by forming Schottky barriers using Ga for the metal. The majority of papers including our work on this subject indicate the Ga Schottky barrier heights on n-GaAs which are anomalously high (1.0 - 1.1 eV). Again this can be explained in terms of the AUDM and an increase in the relative number of Ga_{As} antisite acceptors due to the Ga contact.

Researchers at the Optoelectronic Joint Research Laboratory in Japan have made a detailed study of LaB_6 on GaAs, a system which is of interest for self-aligned gates. LaB_6 was deposited on both chemically cleaned and MBE surfaces. It was found that the Schottky barrier height on n-GaAs moved between positions roughly 0.7 and 0.9 eV beneath the CBM in accord with the amount of excess As at the interface. Both the energy levels and the correlation with As excess are in accord with the AUDM.

IV. Schottky barrier formation for InP interfaces

Parallel to the work on GaAs interfaces, considerable effort has been spent on the study of metal/InP interfaces. The interest in these comes from growth in the number of InP based devices, as well as from a basic interest in the mechanisms responsible for Schottky barrier formation on III-V semiconductors. The earlier studies of these systems by other workers (in particular L. J. Brillson et al. and R. H. Williams) emphasized differences between InP and GaAs interfaces. A dependence of the barrier height on the strength of interfacial reactions has been strongly questioned by our extensive spectroscopic and electrical data. PES studies indicate that neither the extent nor the type of chemical reaction can be strongly correlated with the barrier height. For example, reactive interfaces such as Pd and Cr yield essentially the same I-V barrier height as less reactive interfaces of Cu or Au. Also Schottky barriers with reactive interfaces such as Ni, Mn, Pd, and Al on InP almost completely span the range of I-V barrier heights measured. The interface Fermi level pinning positions during the initial stages of the Schottky barrier formation (submonolayer to several monolayers of coverage) are found to be essentially identical in almost all cases to the interface Fermi level pinning position of thick metal Schottky barriers. We have shown that barrier heights on InP and GaAs span a similar and relatively narrow range of energies of 0.3 eV (although the pinning position is found higher in the gap for InP) and, despite some minor differences, display generally similar trends indicating that physical mechanisms of the barrier formation are not dissimilar. In particular

it seems unlikely that strength of interfacial bonds would play a role. For InP interfaces the Fermi level pinning position is found to fall in a range of 0.3 to 0.6 eV below the CBM and is independent of the type of substrate doping (n- vs p-type). Also consistent with the GaAs results, the small electronegativity metals tend to pin higher in the band gap than the large electronegativity metals.

Our studies indicate that a combination of defects and interfacial states induced by the metal has to be considered to explain Schottky barriers on InP. The low temperature PES data indicate that inhibition of chemical reactions can make MIGS dominant. The Cu/InP system is an example of sucha a case. The pinning at higher temperatures at a different energy is explained by the defect mechanism (it is now believed that charge neutrality level for MIGS and defect level fall at largely different energies 0.35 vs 0.7 eV which allows an experimental identification of mechanism at play in a specific situation. This is contrary to GaAs where these energies are similar). Due to the lack of data on deep levels in InP we did not attempt as yet to propose a specific defect model for InP interfaces (similar to AUDM for GaAs interfaces). An interesting result shedding light on defects responsible for pinning comes from annealing studies of clean surfaces. We found that heating to temperatures below 300 °C produces a reversible change in the band bending on p-InP(110) but not on n-InP(110). It is established that annealing removes P from the surface. Thus removal of P seems to be correlated with the formation of the donor type defects which are necessary to pin p- but not n-type material. No similar effect has been observed on GaAs surfaces, which would suggest differences in the nature of defects. Another difference is the importance of the O.1 eV donor level associated with the oxide which has been emphasized by our studies of nonideal InP interfaces. In the case of GaAs the interfacial oxide has little effect on the barrier height as proven by our detailed PES and electrical studies.

V. Properties of interfaces formed at low temperatures

In the last three years we pioneered the studies of coverage dependent band bending of metal/GaAs and metal/InP interfaces. (A similar research program with complimentary results is in progress at Princeton University by A. Kahn's group.) These experiments have proven to be particularly insightful and provided important new information on the mechanisms of the Schottky barrier formation. The key factor in this research was that by growing the interfaces at low temperatures we are able to reduce the interfacial reactions and inhibit formation of islands. Thus the use of temperature provides a powerful tool to control reactivity and growth morphology. In several cases we are able to obtain interfaces conforming to high standards of ideality (abrupt, epitaxial and nonreactive). These ideal types of systems are practically the only ones which theorists can model. Until recently there was a dramatic mismatch between systems that could be treated theoretically and those that could be realistically produced experimentally. Large progress in understanding the physics of interfaces is thus expected as the result of these studies. Interestingly, for most of the interfaces studied by us, the results systematically indicate large differences between low temperature and high temperature pinning patterns. This shows that reactions and/or growth morphologies affect rectifying barrier heights in an important way. The smallest difference in the temperature pinning patterns are seen for strongly reactive systems (e.g., Ti/GaAs) where reaction is not inhibited at lower temperature. This points out that interfacial reactions are the leading cause for the formation of defects pinning the Fermi level. In reactive systems where low temperature reactions can be completely inhibited, another mechanism has to be invoked to explain the pinning. Our data indicate that in this case metal induced gap states may play a dominant role. We find that in general the interplay between defect and MIGS establishes the barrier height. At very low coverages of metal, as will be discussed below, other mechanisms have to be considered. By now a very broad range of metal/GaAs and InP interfaces has been studied by us at low temperatures. The results are summarized in Table 1.

Table I: Fermi Level Position (E_f - VBM) (eV) and Mechanisms of Schottky Barrier Formation

S.C.	Metal	Thin-PES RT	Thin-PES LT	MIGS	Thick RT	-I.V. An	Chemistry seen RT	Chemistry seen LT	Suggested Dominant mechanism RT	Suggested Dominant mechanism LT
InP	Ag	0.95	0.7	0.7	0.8	--	Y	No	D/M	M
	Cu	0.95	0.95	0.7	0.9	--	Y	Y	D	D
GaAs		0.73(n)								
	Cs	0.5(p)	0.78	0.5	0.65[a]	--	No	No	D	M
		0.75(n)				Ohmic				
	In	0.5(p)	0.56	0.5	0.7[d]	n-GaAs	No	No	D	M
		0.75(n)								
	Ga	0.5(p)	0.56	0.5	~0.3[c]	--	No	No	D	M
		0.75(n)								
	Al	0.5(p)	~0.6	0.5	0.65	0.55	Y	Y	D	-
	Sn	0.6	0.56	0.5	0.65	-	Chemisorp		M/D	M
	Au	0.5	0.52	0.5	0.5	0.6	Y	No	D/M	M
		0.65(n)								
	Ag	0.5(p)		0.5	0.5	0.5	No	No	M/(D)	M
	Cu	0.55	0.52	0.5	0.5	-	Y	Y	D/M	D/M
	Ni	0.5(0.7)	0.49	0.5	0.7	-	Y	Y	D/M	D/M
	Pd	0.45	0.42	0.5	0.55	-	Y	Y	D/M	D/M
	Mn	0.63	0.63	0.5	0.7	-	Y	Y	D/M	D/M
	Cr	0.65	0.61	0.5	0.65	0.65	Y	Y	D/M	D/M
	Ti	0.7	0.77	0.5	0.7	0.6	Y	Y	D	D

VI. Band bending at ultra low coverages of metal ($\varphi << 1$ ML). Role of growth morphology in the formation of rectifying barriers.

With a specially designed evaporator we were able to study band bending from metal coverages as low as 10^{-4} ML. This allowed us to get a better understanding of the processes at the early stages of the Schottky barrier formation. For most metals the band bending at low coverages has proven strongly to depend on the substrate temperature. In general, at low temperature on p-GaAs substrates covered with metals, the Fermi level shifts more readily with metal coverage. The opposite is found on n-GaAs where a negligible initial band bending is observed for decreased temperature. The asymmetry of band bending seen only at low temperatures is caused by and related to the temperature dependence of the overlayer growth morphology. As discussed in the previous section, differences in the final pinning position depend mostly on the temperature dependent reactivity. Further it was proven by us and by others that because of the decreased surface mobility that accompanies low temperature, the formation of clusters could be completely inhibited and the overlayer can grow in the form of individual isolated atoms. The observation that the electropositive metal atoms act as donors explains the observed asymmetry in the low temperature data. Another band bending feature observed for p-GaAs interfaces grown at low temperature is the overshoot, that is, the amount by which band bending at intermediate coverages exceeds the final thick coverage band bending. We find that the overshooting energies are inversely proportional to the first ionization potential of the overlayers atoms (or another characteristic of the metal atoms like electronegativity or work function). This is again in perfect accord with the proposed model in which extrinsic interface states of the donor type are supplied by isolated atoms at the early stage of chemisorption. It is interesting to note that for few metals which also display pronounced overshooting on p-GaAs also at room temperature, the chemisorption occurs in the form of isolated atoms independent of temperature. The best example of this is Cs. Analysis of the

band bending shows that Cs atoms are fully ionized at the early stage of the Schottky barrier formation. A different behavior is found for systems or growth conditions which favor clustering. In these cases the band bending corresponds to the transfer of only a small fraction of the electron to the substrate and is proportional to the logarithm of coverage rather than parabolic law. Part of this may be due to the exothermic cluster induced interfacial reactions which produce compensating centers. However, in cooperation with Prof. S. Doniach [ref. 49] we have shown that yet another mechanism based on screening of the interface states by metallic clusters has to be considered. The key to this model is that screening depends on the size of growing clusters. The increase of the coulomb energy of the complex which limits the band bending (interface states and clusters) is proportional to the square of the transferred charge. Qualitative modelling using this mechanism for the clustered Al and Ag/GaAs(110) interfaces has proved to realistically represent our experimental data.

Another aspect of low coverage studies of clustering systems involves the issue of lateral homogeneity of the band bending. Our careful core level lineshape studies show no evidence of an inhomogeneous surface potential for any doping of the GaAs substrate or metal coverage, even when the depletion length is comparable with the average cluster spacing. The inhomogeneity of the band bending is clearly expected in case of laterally nonuniform distribution of interface states (responsible for band bending). Although this important observation seems to be at odds with most models of the Schottky barrier formation, we provide a feasible interpretation in terms of the defect model assuming that the nature of the defect states depends on the position of the Fermi level. This possibility has been suggested in recent theoretical works.

VII. Oxidation and laser enhanced oxidation of GaAs and InP

The understanding of the oxidation of GaAs and InP is of great importance in device applications. Our new high resolution photoemission data indicates greater variation in oxygen bonding sites for both gallium arsenide and indium phosphide than had been supposed. Oxygen chemisorption is nevertheless confined to the first two or three atomic layers of the semiconductor. Second, for indium phosphide the indium oxides formed are responsible for the unusual changes in surface band bending as oxide coverage increases. This influence of indium oxides explains a large class of exceptions to theories on Fermi level pinning and Schottky barrier formation on compound semiconductors.

Several key facts are revealed about the oxygen chemisorption reaction mechanism for gallium arsenide by comparing oxygen uptake kinetics under different reaction conditions. While the sticking coefficient of molecular oxygen can be increased more than two orders of magnitude by heating the sample or illuminating the surface with visible light, a substantially smaller chemisorption activation energy and photoenhancement effect are seen for nitrous oxide, a more weakly bound molecule. This correlation shows that dissociation of oxygen molecules physisorbed on the surface is a major rate-limiting reaction step and is also the step which is enhanced by visible light. The absence of any dependence on sample temperature or doping type in light-assisted chemisorption of molecular oxygen furthermore indicates a nonthermal enhancement mechanism involving both electrons and holes, possibly through surface recombination. For detailed technical information see Ref. 11, 30, 40, 51, 58 and #2 on the to be published list.

VIII. III-V semiconductor heterojunctions

We performed studies of GaAs and InP heterojunctions with Si and Ge. Heterojunctions are increasingly important in device applications. The understanding of valence band discontinuities is thus of critical importance. Our PES studies indicate that chemistry and band bending must be known before valence band discontinuity can be

correctly established. To obtain dependable values of discontinuities, we performed quantitative analysis of the core level spectra by fitting theoretical lineshapes to the data consisting of several superimposed components. The components which are identified provide information on the position of the Fermi level at the surface, surface core level shifts, overlayer growth mode and the nature of chemical reactions as the overlayer is grown.

The chemical reactions at the Ge/InP interface depend on growth temperature and have a surprising effect on the Fermi level position at the interface. When the Ge/InP interface is grown at 20° C, indium segregates to the surface of the overlayer leaving a heavy concentration of phosphorous intermixed in the overlayer. The phosphorous is an n-type dopant for Ge and the heavy doping concentration significantly affects the band bending making the contact ohmic. This is supported by modelling of the charge and potentials in the surface region.

This data indicate that cross doping may be an important mechanism in the formation of ohmic contacts to the III-V materials. This is substantiated by observation that Ge or Si (i.e. species doping substrate n-type) are constituents of most ohmic contacts to GaAs. For Ge/InP and Si/InP dependable values for the valence band discontinuity were obtained only at 280°C, because of segregated indium (for Ge/InP) and poor overlayer properties (for Si/InP) which obscure the valence band maximum at 20°C. At 280°C substrate temperature, the valence band of Si deposited on InP is 0.7 ± 0.1 eV higher than that of the substrate, and for Ge on InP it is 0.65 ± 0.1 eV higher than that of the substrate.

The understanding of the Si/GaAs heterojunction promises to provide a myriad of new device possibilities by combining the industrially important Si and GaAs technologies on the same chip. While most previous heterojunction studies have focused on a small set of interfacial properties, we have combined electronic, structural, and chemical measurements to study the correlations between these properties and to fully characterize this heterojunction. In situ photoemission, polarization dependent surface extended x-ray

absorption fine structure, near edge structure, low energy electron diffraction and Auger electron spectroscopy were used to characterize on the atomic scale the chemistry, morphology, band bending, valence band discontinuity, crystalline order and overlayer strain during the initial stages of growth. By varying the growth temperature we were able to control the overlayer crystalline quality and the importance of kinetic barriers. In general we found the interface to laminar and abrupt to within one or two atomic layers with chemical reactions confined to this interfacial region. High temperature growths resulted in epitaxial overlayers while room temperature growth produced amorphous material with a large density of defect states in the band gap. The valence band discontinuity was found to be independent of the anisotropic strain and crystalline order of the overlayer. The surface Fermi level appeared to be pinning at approximately 0.7 and 0.9 eV below the CBM for n- and p-type GaAs substrates, respectively. This behavior can be most readily explained by the unified or advanced defect model. The valence band discontinuity was found to be 0.23 ± 0.1 eV for all growth conditions except for room temperature growths for which a large density of defect states are present in the band gap. The 375°C growths remained crystalline at all coverages with dislocations forming for coverages below 4 ML and completely relieving the strain for 16 ML coverages. The strain in the thin overlayers did not produce observable splittings of the valence bands. Room temperature and 300°C growths were amorphous.

IX. Conclusions and some possibilities for future work.

In conclusion we found very strong evidence for the pinning of the Fermi level to be determined by defects at the metal/semiconductor interface. These defects are directly related to the crystal stoichiometry. We propose that anion antisite defects, partly compensated by cation antisite defects, determine the pinning positions observed for metal contacts on state-of-the-art bulk GaAs crystals which are grown from the As rich side of the phase diagram. There is evidence that a similar mechanism might apply for other

compound semiconductors such as InP. To further explore this mechanism it is important to control the concentrations of the native defects through the stoichiometry of the substrate. In the future our work will be extended to good quality Ga rich crystals. Ohmic contacts or more generally Schottky barriers with controlled barrier height constitute an important class of GaAs interfaces both practically and conceptually. Our experimental data as well as computer modelling indicates that the properties at these interfaces can be explained by cross doping of the substrate and the metal. This acknowledges the importance of shallow defects in the more general defect model of the Schottky barrier formation. This phenomenon will also be studied in the future.

Athough defects seem to dominate for practical interfaces, other mechanisms could play an important role if interfaces could be grown under more favorable conditions. In particular there are strong indications that, for nonreactive interfaces grown at low temperatures, MIGS dominate. In general we expect that the properties of the interfaces will be defined by an interplay between these mechanisms. Studies with better control of growth and reactions initiated under our new proposal should define conditions under which each of the mechanisms becomes dominant.

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